

## GOLF BALL HAVING A MECHANICALLY INTERLOCKED COMPONENT

### Field of the Invention

The present invention pertains to the golf ball art, and, more particularly, to a new golf ball with a cover or intermediate layer mechanically interlocked to the core.

### Description of Related Art

Golf balls have typically been divided into four types based on the construction of the balls. The first type of ball to be developed was a one-piece golf ball that was essentially constructed of the same material throughout the entire ball. To improve performance, the second type of golf ball was then developed. This ball consists of an elastomeric core around which a polymeric cover is encapsulated. This is referred to as a two-piece ball. A three-piece or wound ball comprises an elastomeric core around which an elastomeric thread is wound and a tough, yet resilient, cover over the core and thread.

The quest to continue to improve the performance of the golf ball led to the development of the fourth type of ball, the non-wound, multi-layered ball. This type of ball typically includes an elastomeric core surrounded by one or more intermediate layers and a tough cover. Traditionally, each component has had a different composition from the others. In addition, the outer surface of the core and the inner and outer surfaces of the intermediate layers are usually smooth. Such a smooth interface between spherical surfaces results in an inefficient transfer of energy between the layers as well as poor adhesion between the layers.

This inefficiency of energy transfer and poor adhesion results in problems with the main purpose of the golf ball, its playability. When a golf club strikes the outer surface of the golf ball cover, only a portion of the entire sphere is contacted in receiving energy. This energy is transferred to each layer of the ball to the core. Because only a portion of the outer cover initially receives energy, portions of each intermediate layer and the core that are linearly related to the portion of the cover receiving the direct

contact are critical to the transfer of energy. The smooth interfaces often poorly transfer this energy, resulting in a lower total energy transfer to the entire golf ball from the club. This lower energy transfer may result in a shorter travel distance for the ball, less spin or reduction of other similar playability characteristics. It may also result in a cover not adhering properly to a core, which results in poor durability of the golf ball.

A way to eliminate this problem is to change the smooth interfaces of the golf ball components in a manner that allows for better adhesion and a more efficient energy transfer. Some attempts at such a solution have been made. For example, U.S. Patent No. 5,984,807 issued to Ywai et al. and U.S. Patent No. 5,836,834 issued to Masutani et al. disclose the use of solid, geometrically symmetrical projections on the core of a golf ball to improve the interface between the core and its adjacent layer. U.S. Patent No. 5,820,485 issued to Hwang teaches the use of solid, geometrically symmetrical solid protrusions on an intermediate layer to improve energy transfer to the core. U.S. Patent No. 6,066,054 issued to Masutani discloses the use of projections on the inner surface of the cover layer of the golf ball to improve playability characteristics. The inventions of the prior art, however, do not provide the optimum adhesion or mechanical interlock between the layers, or the optimum energy transfer, leading to the best playability characteristics.

Accordingly, it is desirable to develop a new golf ball that would overcome the foregoing difficulties by providing better adhesion and a more efficient transfer of energy throughout the ball.

### **Summary of the Invention**

In accordance with one embodiment of the present invention, a golf ball with mechanically interlocked components is disclosed. The golf ball includes a core and a cover layer disposed about the core. At least one intermediate layer may optionally be disposed between the core and the cover layer. At least one of the cover and optional intermediate layer is mechanically interlocked to the core.

In accordance with another embodiment of the present invention, a golf ball with mechanically interlocked components is disclosed. The golf ball includes a core, a

mantle or intermediate layer disposed about the core, and a cover layer disposed about the mantle layer. The mantle layer is mechanically interlocked with the core.

One advantage of the present invention is that the mechanical interlock between the core and the cover or mantle layer creates improved adhesion and an improved energy transfer, resulting in improved playability characteristics.

Still further advantages of the present invention will become apparent to those of ordinary skill in the art upon reading and understanding the following detailed description of the preferred embodiments.

### **Brief Description of the Drawings**

The invention may take form in certain parts and arrangements of parts, preferred embodiments of which will be described in detail in the specification and merely illustrated in the accompanying drawings which form a part thereof, and wherein:

FIGURE 1 is a cross-sectional view of one embodiment of a golf ball in accordance with the present invention;

FIGURE 2 is a cross-sectional view of a second embodiment of a golf ball in accordance with the present invention;

FIGURE 3 is an exploded sectional view of a portion of the golf ball of FIGURE 1;

FIGURE 4 is a front view, partially in section, of a third embodiment of a golf ball in accordance with the present invention; and

FIGURE 5 is a front view, partially in section, of a fourth embodiment of a golf ball in accordance with the present invention.

### **Detailed Description of the Preferred Embodiments**

Turning now to the drawings, which are provided for the purpose of illustrating the invention and not limiting the same, with reference to FIGURE 1, a golf ball **10** includes a core **12** and a cover **14** disposed about the core **12**. The core **12** has small holes or voids **16**, some of which are undercut, extending inward and running across its outer surface. This configuration of a rough core surface and a cover layer disposed on the core creates an improved interface between the core and the cover with improved adhesion and a more efficient ability to transfer energy. The voids **16** may be formed in

the same processing step as the core **12** or a different step, as will be described below. Each of the voids **16** is randomly placed on the core surface and may vary in size. Since the voids **16** are randomly formed, as further described below, the distance between each void **16** will vary.

Turning now to FIGURE 2, a golf ball **18** according to the present invention is shown. The golf ball **18** includes a core **20** and a cover **22**, as well as at least one intermediate layer **24**. In this embodiment, the core **20** is a dual core having an inner or central core **21** and an outer core or core layer **23**. Particular note is made that although only one intermediate layer **24** is illustrated, more than one intermediate layer may be present between the core **20** and the cover **22**. It is to be understood that the present invention will be described with reference to one mantle or intermediate layer **24**, but any number of additional mantle or intermediate layers are anticipated to be included. The core **20** includes small holes or voids **26** extending inward and running across its outer surface. The voids **26** may be formed in the same processing step as the core **20** or a different step, as will be described below. Each of the voids **26** is randomly placed on the core surface and may vary in size. Since the voids **26** are randomly formed, as further described below, the distance between each void **26** will vary.

Turning now to FIGURE 3, the voids **16** in the core **12** are more clearly shown. The core **12** has an outer surface **32** that defines indentations or voids **16**. The cover layer **14** has an inner surface **34** that defines slight projections **44** that are formed as the cover layer fills the indentations or voids **16** in the core **12**. Thus, the contact surface area between the core and cover of the golf ball is maximized, thereby forming a mechanical interlock and promoting improved adhesion and an increased energy transfer interface between the layers. This results in a greater response by the entire ball to kinetic energy, such as a hit by a golf club, in turn creating a more responsive ball with better playability characteristics.

Although only a two-piece golf ball is shown in FIGURE 3, the same is true for a multi-layer golf ball such as the golf ball of FIGURE 2. For example, when the core **20** includes voids **26** in the outer core **23**, the inner surface **25** of the mantle layer **24** is in proximate contact with the outer core **23** and defines the corresponding projections.

Although the mechanical interlock is only shown between two layers, it is understood that it may be present in multiple layers. For example, for the golf ball shown in FIGURE 2, both the inner core **21** and the outer core **23** may have holes or voids to promote adhesion between the layers.

The cores, intermediate layers and cover layers of the present invention are preferably made according to various molding techniques, such as compression molding, casting, injection molding and reaction injection molding, although any method known to one skilled in the art may be used. Typically, the core is molded into a spheroid shape and any intermediate layers are molded about the core and the cover layer (or layers) is then molded about the final intermediate layer. The holes or voids on the core surface or outer core surface may be made in the same forming step as the core, or they may be formed in a second step, as discussed below. The forming techniques, as mentioned above, compression molding, casting, injection molding and reaction injection molding, may be used separately or in combination for each component of the golf ball. For example, the core may be formed by compression molding, an intermediate layer formed by injection molding, and the cover layer by reaction injection molding, two or more layers may be made by the same process, or all of the components may be formed using the same process.

The golf balls of the invention are formed using a "lost salt process" to create surface voids in the core and/or core layer. Some or all of the surface voids have undercuts, allowing the mantle or cover material to flow into the undercuts when molded, thus locking the mantle or cover into the core to improve adhesion between the layers.

As used herein, the lost salt process refers to a process where the core material, such as the slug or preform, is coated with a particulate material. The particulate material can be any material known in the art that will easily be removed with an aqueous or non-aqueous solvent. Examples of particulate materials suitable for use in the invention include, but are not limited to, crystalline and amorphous shaped particles, such as salts, sugars, agar, gelatin, polyvinyl alcohol, thermoplastic particulate, and the like. Combinations of any of these materials may also be used. The core material may be coated in any manner, such as by rolling the slug or preform in the particulate, or any

other method known in the art. The coated slugs or preforms are then molded into cores, preferably spherical cores, using molding techniques known in the art, such as compression molding. The molded cores have a relatively smooth outer surface with the particulate molded into the surface of the core. The cores are then flushed or washed with an aqueous or non-aqueous solvent and dried, preferably blown dry. Preferred solvents include, but are not limited to, water and organic solvents such as alcohol, acetone, methyl ethyl ketone, toluene, naptha, and the like, but other solvents may be used as long as they do not damage or change the core matrix. By washing the cores, the particulate is removed, and a large number of voids or small holes remain on the surface of the cores. The size of the voids will be determined by the size of the particulate used, but will generally be very small. In a preferred embodiment, the particulate material has a size of from about 5 to about 400 mesh U.S. standard size, preferably about 10 to about 200, more preferably about 20 to about 60 mesh U.S. standard size.

In an alternate embodiment, hollow microspheres, such as ceramic, glass, phenolic or thermoplastic microspheres, may also be used to coat the core material. After molding the hollow microspheres into the core surface, the cores can be lightly ground on a centerless grinding machine known in the art. This will expose small hemispherical holes on the surface of the core. The hemispherical holes on the surface of the core or core layer will look similar to the voids **16** and **26** shown in FIGURES 1 to 3. When a cover is disposed on the core, the cover and core will be mechanically interlocked.

In another embodiment, small fibers, such as polyvinyl alcohol fibers, can be woven into a fabric, and the fabric can be used in the golf ball. In this embodiment, the fabric is inserted into the mold cavities and then a core is molded using standard molding techniques, such as compression molding. After molding, the fabric will then be molded onto the core surface. The fabric can be dissolved in a solvent, such as water, to remove the fibers, creating a surface similar to a wound golf ball core surface. Any suitable solvent may be used, as long as it dissolves the fibers but does not change the core properties or core matrix. The fibers of the fabric create depressions or impressions in the surface of the core or core layer after the fabric is dissolved and

washed away. When a mantle or cover layer is then molded around the core, the mantle or cover layer will be interlocked with the core because the mantle or cover layer will fill in the depressions in the core surface, thereby interlocking the core and the mantle or cover layer.

Turning now to FIGURE 4, a golf ball **58** having a core **52** and a cover layer **54** disposed on the core **52** is shown. The core **52** has an outer surface **60** that defines depressions **56** formed when the fabric is dissolved and removed or washed away. The cover layer **54** fills the depressions **56** in the core **52**. Thus, the contact surface area between the core and cover of the golf ball is maximized, thereby forming a mechanical interlock and promoting improved adhesion and an increased energy transfer interface between the layers. This results in a greater response by the entire ball to kinetic energy, such as a hit by a golf club, in turn creating a more responsive ball with better playability characteristics. The cover layer **54** may be a single layer or a multi-layer cover as described herein.

Turning now to FIGURE 5, a golf ball **68** having a core **62**, a core layer **63** and a cover layer **64** disposed on the core layer **63** is shown. The core layer **63** has an outer surface **70** that defines depressions **66** formed when the fabric is dissolved and removed or washed away. The cover layer **64** fills the depressions **66** in the core layer **63**. Thus, the contact surface area between the core layer and cover of the golf ball is maximized, thereby forming a mechanical interlock and promoting improved adhesion and an increased energy transfer interface between the layers. The cover layer **64** may be a single layer or a multi-layer cover as described herein.

These processes are advantageous because they allow the layer covering the core, whether it is a mantle or cover layer, to be interlocked with the core because the material can flow into the voids, depressions, and/or undercuts formed in the core surface. Molds having internal projections, such as those of the prior art, are not able to produce undercuts, therefore the degree of mechanical locking between the components is not as great.

The core and/or intermediate layer(s) (also known as mantle layers) and/or cover layer(s) may be formed from a thermoset material, a thermoplastic material, or combinations thereof, as known to one skilled in the art.

A wide array of thermoset materials can be utilized in any of the layers of the present invention. Examples of suitable thermoset materials include butadiene or any natural or synthetic elastomer, including metallocene polyolefins, polyurethanes, silicones, polyamides, polyureas, or virtually any irreversibly cross-linked resin system. Similarly a polybutadiene elastomer could be further used. It is also contemplated that epoxy, phenolic, and an array of unsaturated polyester resins could be utilized.

The thermoplastic materials used in the present invention golf ball layers include a wide assortment of thermoplastic materials. Examples of typical thermoplastic materials for incorporation in the golf balls of the present invention include, but are not limited to, ionomers, polyurethane thermoplastic elastomers, and combinations thereof. It is also contemplated that a wide array of other thermoplastic materials could be utilized, such as polysulfones, fluoropolymers, polyamide-imides, polyarylates, polyaryletherketones, polyaryl sulfones/polyether sulfones, polybenzimidazoles, polyether-imides, polyamides, liquid crystal polymers, polyphenylene sulfides; and specialty high-performance resins, which would include fluoropolymers, polybenzimidazole, and ultrahigh molecular weight polyethylenes.

Additional examples of suitable thermoplastics include metallocenes, polyvinyl chlorides, acrylonitrile-butadiene-styrenes, acrylics, styrene-acrylonitriles, styrene-maleic anhydrides, polyamides (nylons), polycarbonates, polybutylene terephthalates, polyethylene terephthalates, polyphenylene ethers/polyphenylene oxides, reinforced polypropylenes, and high-impact polystyrenes.

Any or all of the previously described components in the layers of the preferred embodiment golf balls of the present invention may be formed in such a manner, or have suitable fillers added, so that their resulting density is decreased or increased. For example, any of the components in the cores and/or mantle layers could be formed or otherwise produced to be light in weight. For instance, the components could be foamed, either separately or *in situ*. Related to this, a foamed lightweight filler agent may be added. In contrast, any of these components could be mixed with, or otherwise receive, various high density filler agents or other weighting components such as relatively high density fibers or particulate agents in order to increase their mass or weight.



The cores generally have a weight of about 25 to 40 grams and preferably about 30 to 40 grams, although this may vary depending on the desired properties of the core and finished golf ball. The cores can be molded from materials noted herein. For example the core can be molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an ethylenically unsaturated carboxylic acid such as zinc mono- or diacrylate or methacrylate. To achieve higher coefficients of restitution and/or to increase hardness in the core, the manufacturer may increase the amount of zinc diacrylate co-agent. In addition, larger amounts of metal oxide such as zinc oxide may be included in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Non-limiting examples of other materials which may be used in the core composition include compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiator catalysts such as peroxides are admixed with the core composition so that on the application of heat and pressure, a curing or crosslinking reaction takes place.

The cores and intermediate layers of the present invention are preferably formed by compression molding techniques. However, it is fully contemplated that liquid injection molding, blow molding or transfer molding techniques could be utilized, in addition to all of the previously described forming techniques.

Additionally, the core and/or intermediate layer compositions of the invention may be based on polybutadiene, natural rubber, metallocene catalyzed polyolefins, polyurethanes, other thermoplastic or thermoset elastomers, and mixtures of one or more of the above materials with each other and/or with other elastomers.

In a preferred embodiment core, it is preferred that a base elastomer having a relatively high molecular weight is used. Polybutadiene has been found to be particularly useful because it imparts to the golf balls a relatively high coefficient of restitution. Polybutadiene can be cured using a free radical initiator such as peroxide, or it can be sulfur cured. A broad range for the molecular weight of preferred base elastomers is from about 50,000 to about 500,000. A more preferred range for the molecular weight of the base elastomer is from about 100,000 to about 500,000. As a base elastomer for the core composition, cis-1-4-polybutadiene is preferably employed,

or a blend of cis-1-4-polybutadiene with other elastomers may also be utilized. Furthermore, the core may be comprised of a crosslinked natural rubber, EPDM, metallocene-catalyzed polyolefin, or another crosslinkable elastomer.

When polybutadiene is used for golf ball cores, it commonly is crosslinked with an unsaturated carboxylic acid co-crosslinking agent. The unsaturated carboxylic acid component of the core composition typically is the reaction product of the selected carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin, and the like. Preferably, the oxides of polyvalent metals such as zinc, magnesium and cadmium are used, and most preferably, the oxide is zinc oxide.

Exemplary of the unsaturated carboxylic acids which find utility in the core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and the like, and mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually, from about 5 to about 40, and preferably from about 15 to about 30 parts by weight of the carboxylic acid salt, such as zinc diacrylate, is included in the core composition. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible.

The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used herein refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes cross linking of the elastomers by the metal salt of the unsaturated carboxylic acid. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators include peroxides, persulfates, azo compounds and hydrazides. Peroxides, which are readily commercially available, are conveniently used in the present invention, generally in amounts of from about 0.1 to about 10.0 and preferably in amounts of from about 0.3 to about 3.0 parts by weight per each 100 parts of elastomer.

Exemplary of suitable peroxides for the purposes of the present invention are dicumyl peroxide, n-butyl 4,4'-bis (butylperoxy) valerate, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane, di-t-butyl peroxide and 2,5-di-(t-butylperoxy)-2,5 dimethyl hexane

and the like, as well as mixtures thereof. It will be understood that the total amount of initiators used will vary depending on the specific end product desired and the particular initiators employed.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, metal oxides, fatty acids, and diisocyanates and polypropylene powder resin. For example, Papi<sup>®</sup> 94, a polymeric diisocyanate, commonly available from Dow Chemical Co., Midland, Mich., is an optional component in the rubber compositions. It can range from about 0 to 5 parts by weight per 100 parts by weight rubber (phr) component, and acts as a moisture scavenger. In addition, it has been found that the addition of a polypropylene powder resin results in a core which is hard (exhibits high PGA compression) and thus allows for a reduction in the amount of cross linking co-agent utilized to soften the core to a normal or below normal compression.

Furthermore, because polypropylene powder resin can be added to a core composition without an increase in weight of the molded core upon curing, the addition of the polypropylene powder allows for the addition of higher specific gravity fillers, such as mineral fillers. Since the cross linking agents utilized in the polybutadiene core compositions are expensive and/or the higher specific gravity fillers are relatively inexpensive, the addition of the polypropylene powder resin substantially lowers the cost of the golf ball cores while maintaining, or lowering, weight and compression.

Various activators may also be included in the compositions of the present invention. For example, zinc oxide and/or magnesium oxide are activators for the polybutadiene. The activator can range from about 2 to about 30 parts by weight per 100 parts by weight of the rubbers (phr) component.

Moreover, reinforcement agents may be added to the core compositions of the present invention. Since the specific gravity of polypropylene powder is very low, and when compounded, the polypropylene powder produces a lighter molded core, when polypropylene is incorporated in the core compositions, relatively large amounts of higher specific gravity fillers may be added so long as the specific core weight limitations are met. As indicated above, additional benefits may be obtained by the incorporation of relatively large amounts of higher specific gravity, inexpensive mineral

fillers such as calcium carbonate. Such fillers as are incorporated into the core compositions should be in finely divided form, as for example, in a size generally less than about 30 mesh and preferably less than about 100 mesh U.S. standard size. The amount of additional filler included in the core composition is primarily dictated by weight restrictions and preferably is included in amounts of from about 10 to about 100 parts by weight per 100 parts rubber.

The preferred fillers are relatively inexpensive and heavy and serve to lower the cost of the ball and to increase the weight of the ball to closely approach the U.S.G.A. weight limit of 1.620 ounces. However, if thicker cover compositions are to be applied to the core to produce larger than normal (greater than 1.680 inches in diameter) balls, use of such fillers and modifying agents will be limited in order to meet the U.S.G.A. maximum weight limitations of 1.620 ounces. Limestone is ground calcium/magnesium carbonate and is used because it is inexpensive, heavy filler. Ground flash filler may be incorporated and is preferably 20 mesh ground up center stock from the excess flash from compression molding. It lowers the cost and may increase the hardness of the ball.

Fatty acids or metallic salts of fatty acids may also be included in the compositions, functioning to improve moldability and processing. Generally, free fatty acids having from about 10 to about 40 carbon atoms, and preferably having from about 15 to about 20 carbon atoms, are used. Exemplary of suitable fatty acids are stearic acid and linoleic acids, as well as mixtures thereof. An example of a suitable metallic salt of a fatty acid is zinc stearate. When included in the core compositions, the metallic salts of fatty acids are present in amounts of from about 1 to about 25, preferably in amounts from about 2 to about 15 parts by weight based on 100 parts rubber (elastomer). It is preferred that the core compositions include stearic acid as the fatty acid adjunct in an amount of from about 2 to about 5 parts by weight per 100 parts of rubber.

Diisocyanates may also be optionally included in the core compositions. When utilized, the diisocyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts rubber. Exemplary of suitable diisocyanates is 4,4'-diphenylmethane diisocyanate and other polyfunctional isocyanates known in the art.

Furthermore, the dialkyl tin difatty acids set forth in U.S. Patent No. 4,844,471, the dispensing agents disclosed in U.S. Patent No. 4,838,556, and the dithiocarbamates set forth in U.S. Patent No. 4,852,884 may also be incorporated into the polybutadiene compositions of the present invention. The specific types and amounts of such additives are set forth in the above identified patents, which are incorporated herein by reference.

As noted, cores according to the present invention can be manufactured using techniques such as injection molding, blow molding, compression molding and reaction injection molding, or any other technique known to one skilled in the art.

The cover layer(s) of golf balls according to the present invention may comprise any material suitable for use in a golf ball cover, such as those previously described. Examples of preferred materials include, but are not limited to, ionomer resins, polyurethane materials, and nylon compositions.

It is appreciated that the following described materials may be used in a single layer cover or a multi-layer cover as any of an outer cover layer or an inner cover layer. Additionally, the cover materials described herein are also suitable for forming an intermediate or mantle layer.

With respect to a preferred ionomeric cover composition of the invention, ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability, and flight characteristics, various ionomeric resins sold by E.I. DuPont de Nemours & Company under the trademark Surlyn<sup>®</sup> and by the Exxon Corporation (see U.S. Patent No. 4,911,451, incorporated herein by reference) under the trademarks Escor<sup>®</sup> and Iotek<sup>®</sup>, have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or synthetic) rubbers.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid or maleic acid. In some instances, an additional softening comonomer such as an acrylate can also be included to form a terpolymer. The pendent ionic groups in the ionomeric resins interact to form ion-rich aggregates contained in a non-polar polymer matrix. The metal ions, such as sodium, zinc, magnesium, lithium, potassium, calcium,

and the like, are used to neutralize some portion of the acid groups in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, for example, improved durability, for golf ball construction over balata.

The ionomeric resins utilized to produce cover compositions can be formulated according to known procedures such as those set forth in U.S. Patent No. 3,421,766 or British Patent No. 963,380, with neutralization effected according to procedures disclosed in Canadian Patent Nos. 674,595 and 713,631, all of which are hereby incorporated by reference, wherein the ionomer is produced by copolymerizing the olefin and carboxylic acid to produce a copolymer having the acid units randomly distributed along the polymer chain. Broadly, the ionic copolymer generally comprises one or more  $\alpha$ -olefins and from about 9 to about 20 weight percent of  $\alpha$ ,  $\beta$ -ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired.

At least about 20% of the carboxylic acid groups of the copolymer are neutralized by the metal ions (such as sodium, potassium, zinc, calcium, magnesium, and the like) and exist in the ionic state. Suitable olefins for use in preparing the ionomeric resins include ethylene, propylene, butene-1, hexene-1 and the like. Unsaturated carboxylic acids include acrylic, methacrylic, ethacrylic,  $\alpha$ -chloroacrylic, crotonic, maleic, fumaric, itaconic acids, and the like. The ionomeric resins utilized in the golf ball industry are generally copolymers of ethylene with acrylic (for example, Iotek<sup>®</sup>) and/or methacrylic (for example, Surlyn<sup>®</sup>) acid. In addition, two or more types of ionomeric resins may be blended into the cover compositions in order to produce the desired properties of the resulting golf balls.

Examples of suitable cover compositions which may be used in making the preferred embodiment golf balls of the present invention are set forth in detail but not limited to those in U.S. Patent Nos. 6,267,693, and 5,688,869, incorporated herein by reference. Of course, the cover compositions are not limited in any way to those compositions set forth in the patents. The cover layer(s) may include a blend of hard and soft (low acid) ionomer resins such as those described in U.S. Patent Nos. 4,884,814 and 5,120,791, both incorporated herein by reference. Other cover layer(s)

may include those as described in U.S. Patent Nos. 6,210,293; 6,213,894; 6,224,498; and 6,287,217, incorporated herein by reference.

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced spin characteristics produced by the low acid ionomer resin compositions. These include, but are not limited to thermoplastic polyurethanes such as: Texin<sup>®</sup> thermoplastic polyurethanes from Mobay Chemical Co., Pellethane<sup>®</sup> thermoplastic polyurethanes from Dow Chemical Co. and Estane<sup>®</sup> polyester polyurethane from B.F. Goodrich Company; Ionomer/rubber blends such as those in U.S. Patents 4,986,545; 5,098,105 and 5,187,013; Hytrel<sup>®</sup> polyester elastomers from DuPont; and Pebax<sup>®</sup> polyetheramides from Elf Atochem S.A.

Polyurethanes are polymers that are used to form a broad range of products. They are generally formed by mixing two primary ingredients during processing. For the most commonly used polyurethanes, the two primary ingredients are a polyisocyanate (for example, diphenyl methane diisocyanate monomer ("MDI") and toluene diisocyanate ("TDI") and their derivatives) and a polyol (for example, a polyester polyol or a polyether polyol).

A wide range of combinations of polyisocyanates and polyols, as well as other ingredients, are available. Furthermore, the end-use properties of polyurethanes can be controlled by the type of polyurethane utilized, that is, whether the material is thermoset (crosslinked molecular structure) or thermoplastic (linear molecular structure).

Crosslinking occurs between the isocyanate groups (-NCO) and the polyol's hydroxyl end-groups (-OH). Additionally, the end-use characteristics of polyurethanes can also be controlled by different types of reactive chemicals and processing parameters. For example, catalysts are utilized to control polymerization rates. Depending upon the processing method, reaction rates can be very quick (as in the case for some reaction injection molding systems ("RIM")) or may be on the order of several hours or longer (as in several coating systems). Consequently, a great variety of polyurethanes are suitable for different end uses.

Polyurethane has been used for golf balls and other game balls as a cover material. Commercially available polyurethane golf balls have been made of thermoset and thermoplastic polyurethanes. A polyurethane becomes irreversibly "set" when a polyurethane prepolymer is cross linked with a polyfunctional curing agent, such as polyamine and polyol. The prepolymer typically is made from polyether or polyester. Diisocyanate polyethers are preferred for some embodiments because of their water resistance.

The physical properties of thermoset polyurethanes are controlled substantially by the degree of cross linking. Tightly cross linked polyurethanes are fairly rigid and strong. A lower amount of cross linking results in materials that are flexible and resilient. Thermoplastic polyurethanes have some cross linking, but purely by physical means. The crosslinkings bonds can be reversibly broken by increasing temperature, as occurs during molding or extrusion. In this regard, thermoplastic polyurethanes can be injection molded, and extruded as sheet and blown film. They can be used up to about 350°F and are available in a wide range of hardnesses.

Polyurethane materials suitable for the present invention are generally formed by the reaction of a polyisocyanate, a polyol, and optionally one or more chain extending diols. The polyisocyanate is selected, for example, from the group including, but not limited to, diphenyl methane diisocyanate ("MDI"); toluene diisocyanate ("TDI"); xylene diisocyanate ("XDI"); methylene bis-(4-cyclohexyl isocyanate) ("HMDI"); hexamethylene diisocyanate; and naphthalene-1,5,-diisocyanate ("NDI").

Further examples of suitable polyurethanes include polyurethane systems formed via reaction injection molding (RIM). RIM processing to form various layers of a golf ball is described in detail U.S. Patent No. 6,290,614, incorporated herein by reference.

The golf balls of the present invention can be produced, at least in part, by molding processes currently known in the golf ball art. Specifically, golf balls can be produced by injection molding or compression molding an intermediate layer about molded cores to produce an intermediate golf ball generally having a diameter of about 1.50 to 1.67 inches. The cover layer is subsequently molded over the intermediate layer to produce a golf ball having a diameter of 1.680 inches or more. If no intermediate layer is desired, the cover layer can be molded directly over the core. For



golf balls having a dual core, a core layer or layers is molded over a center core component to form the core, and the intermediate and/or cover layer(s) are then molded over the core.

For polyurethane components, a preferred method of forming the polyurethane component is by reaction injection molding ("RIM"). RIM is a process by which highly reactive liquids are injected into a closed mold, mixed usually by impingement and/or mechanical mixing in an in-line device such as a "peanut mixer," where they polymerize primarily in the mold to form a coherent, one-piece molded article. The RIM processes usually involve a rapid reaction between one or more reactive components such as polyether - or polyester - polyol, polyamine, or other material with an active hydrogen, and one or more isocyanate - containing constituents, often in the presence of a catalyst. The constituents are stored in separate tanks prior to molding and may be first mixed in a mix head upstream of a mold and then injected into the mold. The liquid streams are metered in the desired weight to weight ratio and fed into an impingement mix head, with mixing occurring under high pressure, for example, about 1500 to 3000 psi. The liquid streams impinge upon each other in the mixing chamber of the mix head and the mixture is injected into the mold. One of the liquid streams typically contains a catalyst for the reaction. The constituents react rapidly after mixing to gel and form polyurethane polymers. Polyureas, epoxies, and various unsaturated polyesters also can be molded by RIM.

In addition to the above noted ionomers and non-ionomers, compatible additive materials may also be added to produce the cover compositions of the present invention. These additive materials include dyes (for example, Ultramarine Blue™ sold by Whitaker, Clark, and Daniels of South Plainfield, NJ), and pigments such as white pigments such as titanium dioxide (for example Unitane™ 0-110) zinc oxide, and zinc sulfate, as well as fluorescent pigments. As indicated in U.S. Patent 4,884,814, the amount of pigment and/or dye used in conjunction with the polymeric cover composition depends on the particular base ionomer or non-ionomer mixture utilized and the particular pigment and/or dye utilized. The concentration of the pigment in the polymeric cover composition can be from about 1% to about 10% as based on the weight of the base ionomer or non-ionomer mixture. A more preferred range is from

about 1% to about 5% as based on the weight of the base ionomer or non-ionomer mixture. The most preferred range is from about 1% to about 3% as based on the weight of the base ionomer or non-ionomer mixture. The most preferred pigment for use in accordance with this invention is titanium dioxide.

Moreover, since there are various hues of white, such as blue white, yellow white, and the like, trace amounts of blue pigment may be added to the cover stock composition to impart a blue white appearance thereto. However, if different hues of the color white are desired, different pigments can be added to the cover composition at the amounts necessary to produce the color desired.

In addition, it is within the purview of this invention to add to the cover compositions of this invention compatible materials that do not affect the basic novel characteristics of the composition of this invention. Among such materials are antioxidants (for example, Santonox<sup>®</sup> R), antistatic agents, stabilizers and processing aids. The cover compositions of the present invention may also contain softening agents, such as plasticizers, and reinforcing materials such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

Furthermore, optical brighteners, such as those disclosed in U.S. Patent No. 4,679,795, herein incorporated by reference, may also be included in the cover composition of the invention. Moreover, since many optical brighteners are colored, the percentage of optical brighteners utilized must not be excessive in order to prevent the optical brightener from functioning as a pigment or dye in its own right.

The various cover composition layers of the present invention may be produced according to conventional melt blending procedures or other conventional procedures. For example, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury<sup>®</sup> mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the

barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, may be added and uniformly mixed before initiation of the molding process.

Often, fillers are used in one or more layers of a golf ball. If desired, any layer of the golf ball may contain at least one part by weight of a filler. Fillers preferably are used to adjust the density, flex modulus, mold release, and/or melt flow index of a layer. More preferably, at least when the filler is for adjustment of density or flex modulus of a layer, it is present in an amount of at least five parts by weight based upon 100 parts by weight of the layer composition. With some fillers, up to about 200 parts by weight probably can be used.

A density adjusting filler according to the invention preferably is a filler which has a specific gravity which is at least 0.05 and more preferably at least 0.1 higher or lower than the specific gravity of the layer composition. Particularly preferred density adjusting fillers have specific gravities that are higher than the specific gravity of the resin composition by 0.2 or more, even more preferably by 2.0 or more.

A flex modulus adjusting filler according to the invention is a filler which, when used in an amount of about 1 to 100 parts by weight based upon 100 parts by weight of resin composition, will raise or lower the flex modulus (ASTM D-790) of the resin composition by at least 1% and preferably at least 5% as compared to the flex modulus of the resin composition without the inclusion of the flex modulus adjusting filler.

The layers may contain coupling agents that increase adhesion of materials within a particular layer, such as to couple a filler to a resin composition, or between adjacent layers. Non-limiting examples of coupling agents include titanates, zirconates and silanes. Coupling agents typically are used in amounts of 0.1 to 2 weight percent based upon the total weight of the composition in which the coupling agent is included. Coupling agents and other chemical adhesives may be used in addition to the mechanical interlocking of the invention.

The density-increasing fillers for use in the invention preferably have a specific gravity in the range of 1.0 to 20. The density-reducing fillers for use in the invention preferably have a specific gravity of 0.06 to 1.4, and more preferably 0.06 to 0.90. The flex modulus increasing fillers have a reinforcing or stiffening effect due to their

morphology, their interaction with the resin, or their inherent physical properties. The flex modulus reducing fillers have an opposite effect due to their relatively flexible properties compared to the matrix resin. The melt flow index increasing fillers have a flow enhancing effect due to their relatively high melt flow versus the matrix. The melt flow index decreasing fillers have an opposite effect due to their relatively low melt flow index versus the matrix.

Fillers which may be employed in layers other than the outer cover layer may be or are typically in a finely divided form, for example, in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size, except for fibers and flock, which are generally elongated. Flock and fiber sizes should be small enough to facilitate processing. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations. Examples of fillers that may be used in the invention include, but are not limited to, precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates, metals, metal alloys, tungsten carbide, metal oxides, metal stearates, particulate carbonaceous materials, micro balloons, and combinations thereof.

The foregoing description is, at present, considered to be the preferred embodiments of the present invention. However, it is contemplated that various changes and modifications apparent to those skilled in the art, may be made without departing from the present invention. Therefore, the foregoing description is intended to cover all such changes and modifications encompassed within the spirit and scope of the present invention, including all equivalent aspects.